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**OVER MOLDING OF LIGHTENED AMIDE BLOCK POLYETHER ON THERMOPLASTIC ELASTOMER**

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(56) Prior Art Documents
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**US A 4816345**

(57) Claim

1. A bilayer article comprising a lightened thermoplastic elastomer of the polyetheramide type adhering, by itself, to a non-lightened thermoplastic.

2. Bilayer article according to 1, in which the non-lightened thermoplastic is chosen from polyetheramides, polyetheresters, polyurethanes.

3. Bilayer article according to 1, characterized in that the polyetheramides are polyetheresteramides obtained by polycondensation of aliphatic alpha,omega-dihydroxylated polyamide blocks.

4. Method of joining together, without adhesive, a lightened thermoplastic elastomer of the polyetheramide type and other non-lightened thermoplastics of the same kind or of a different kind,

.../2

characterized in that the joining-together is performed in one operation during the injection of the second material onto the first, this having the function of an insert.

5. Shoe sole comprising a bilayer according to any one of Claims 1 to 3.

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(54) Title: OVER MOLDING OF LIGHTENED AMIDE BLOCK POLYETHER ON THERMOPLASTIC ELASTOMER

(54) Titre: SURMOULAGE DE POLYETHER BLOCK AMIDE ALLEGE SUR UN ELASTOMERE THERMOPLASTIQUE

(57) Abstract

Bilayer object comprising a lightened thermoplastic elastomer of the polyether amide type adhering by itself on a non lightened thermoplastic selected from polyether amides, polyether esters, polyurethanes. The bilayer product obtained by molding the lightened thermoplastic over the compact thermoplastic may be used in the fabrication of shoe soles.

(57) Abrégé

Objet bicouche comprenant un élastomère thermoplastique allégé de type polyétheramide adhérant en lui-même sur un thermoplastique non allégé pouvant être choisi parmi les polyétheramides, polyétheresters, polyuréthannes. Le bicouche, obtenu par surmoulage du thermoplastique allégé sur le thermoplastique compact, peut être employé dans la fabrication des semelles de chaussures.

# OVERMOULDING OF LIGHTENED AMIDE BLOCK POLYETHER ON A THERMOPLASTIC ELASTOMER

The composite which forms the subject of the present invention comprises a lightened thermoplastic elastomer adhering by itself to a compact material consisting of a non-lightened thermoplastic.

The joining of a lightened thermoplastic elastomer to compact thermoplastics of the same kind or of different compositions is, hitherto, obtained by moulding or extrusion followed by cutting-out of the components and then adhesive bonding and pressing of these components.

For example, European Application EP 402,883 describes the use of a lightened thermoplastic elastomer (this may, inter alia, be a copolyetheramide as described in EP 405,227) in the insole of sports shoes. However, the multilayer described is joined together, using a conventional technique, by adhesively bonding the lightened thermoplastic to the compact material.

The advantage of the present invention is to enable the components to be joined together solely by the overmoulding of one onto the other, without the

addition of a tie layer. This cohesion between the materials is made possible by the adhesive properties which polyetheramides in the molten state possess.

European Application EP 197,845 describes a method of joining surfaces together by application of a polyetheramide seal and melting of its surface layer: but the thermoplastic substance which forms the seal is applied in the form of a strip (not of a foam) between two substrates which are not elastomers.

European Application EP 179,700 describes an adhesive composition comprising a polyetheresteramide and its use as a pressure-sensitive adhesive, but here too a foam is not involved.

The invention enables a composite to be produced which consists of a lightened material, possessing a low density, high flexibility and good elastic memory, and of a compact material characterized by its rigidity and its abrasion resistance.

The materials which result from this may be used in sports shoes as soles of the "semi-rigid" type (for football, baseball, etc.) or of the flexible type (for jogging) enabling the insole (for damping) and the external sole (for abrasion resistance and rigidity) to be produced directly.

This complex may also be employed for producing town shoes requiring a damping/flexibility and rigidity/abrasion compromise. This composite may be used for body-protecting articles, such as knee pads

(for skate-boarding), shin pads (for football), elbow pads, insides of cycling helmets.

The bilayer article which forms the present invention is assembled according to the overmoulding technique which consists in injecting a substance onto an insert placed in the bottom of the mould.

The cohesion of the two materials is obtained by the hot-melt and compatibility properties of the overmoulded substance and of the insert. Polyetheramides are very well suited to this overmoulding technique since they possess a wide plasticization range making it possible to optimize the adhesion of the substance to the inserts and to avoid the use of adhesive.

It is preferable to inject the lightened polyether-block-amide onto the compact thermoplastic insert: this overmoulding technique is the most sensible and provides very good results, both from the standpoint of the aesthetic appearance of the finished articles and of the adhesion between the materials; however, the reverse operation (injection of the compact thermoplastic onto the lightened substance) is performed under similar conditions.

The thermoplastic polymer is lightened by incorporating products having the properties of decomposing under the effect of a temperature rise. The gas produced is intimately mixed with the molten substance under the combined effects of temperature,

pressure and shear.

The incorporation of blowing agents will be carried out differently depending on whether they are in liquid/gaseous or solid form.

The injection of liquid or gaseous blowing agents will be performed with the aid of a metering pump in the molten substance, in the region of the nozzle for injecting the polymer.

Solid blowing agents will generally be added to the elastomer granules by mechanically mixing before being introduced into the hopper.

The polyetheramide which is employed as the lightened material may be chosen from random polyetheramides (that is to say formed by the random linking of the various monomer constituents) or block polyetheramides, that is to say formed by blocks having a certain chain length of their various constituents.

Block polyetheramides result from the copolycondensation of polyamide blocks having reactive end groups with polyether blocks having reactive end groups, such as, inter alia:

1) Diamine-terminated polyamide blocks with dicarboxylic-terminated polyoxyalkylene blocks;

2) Dicarboxylic-terminated polyamide blocks with diamine-terminated polyoxyalkylene blocks obtained by cyanoethylation and hydrogenation of polyetherdiols;

3) Dicarboxylic-terminated polyamide blocks with aliphatic alpha,omega-dihydroxylated

polyoxyalkylene or polyetherdiol blocks, the polyetheramides being obtained, in this particular case, from polyetheresteramides.

The composition and manufacture of such block polyetheresteramides have been described in French Patents No. 74/18913 and 77/26678 in the name of the Applicant Company, the contents of which are added to the present description.

Particularly well suited for the implementation of the present invention are the block polyetheresteramides obtained by polycondensation of dicarboxylic polyamide 11 or 12 blocks of molecular weight between 300 and 15,000 with polyoxytetramethylene glycol blocks of molecular weight between 100 and 6,000, with a content of from 95 to 15% by weight of polyamide blocks for 5 to 85% by weight of polyoxytetramethylene glycol.

The compact material formed by a non-lightened thermoplastic may be the same or different from the lightened material; it may be chosen from polyetheramides, polyetheresters, polyurethanes, etc.

Two types of blowing agent have been used:

- exothermic type (Genitron EPC or EPA, from Schering) based on azodicarbonamide which decomposes from a temperature of 165°C upwards;
- endothermic type (Genitron SIC 35/22, from Schering or Hydrocerol B, from BOEHRINGER) containing sodium bicarbonate and decomposing from a temperature

of 160°C upwards.

The endothermic-type blowing agents decompose, of course, under the effect of heat, but this decomposition stops as soon as the heat supply is removed, contrary to the exothermic agents for which the decomposition continues even after removing the heat source and which then require significant cooling. Among other characteristics of the foam obtained with this agent, a highly pronounced surface-skin effect and a very fine cellulation have been observed; the densities of PEBAX lightened by this type of agent are 0.6. It would not be outside the scope of the invention to combine the bilayer of the invention with films, sheets or other layers, of other materials.

The thermoplastics used for the tests are as follows:

- Elastomer A (PEBAX 2533) polyetheresteramide based on polyamide 12 and polytetramethylene glycol in a PA/PE mass ratio = 20/80.
  - Melting point: 135°C
  - Melt index at 235°C/1 kg/2 mm die = 10
  - Shore D hardness = 25
- Elastomer B (PEBAX MX 1205) polyetheresteramide based on polyamide 12 and polytetramethylene glycol in a PA/PE mass ratio = 50/50:
  - Melting point = 147°C

- Melt index at 235°C/1 kg/2 mm die = 10
- Shore D hardness = 40

● Elastomer C (PEBAX 3533) polyetheresteramide based on polyamide 12 and polytetramethylene glycol in a PA/PE mass ratio = 30/70

- Melting point = 144°C
- Melt index at 235°C/1 kg/2 mm die = 9
- Shore D hardness = 35

● Elastomer D (Elastollan 1185 A50) polyetherurethane

- Melting point = 165°C
- Shore D hardness = 35

● Elastomer E (Hytrel 4056) polyetherester

- Melting point = 150°C
- Melt index at 190°C/2.16 kg/2 mm die = 5
- Shore D hardness = 40.

Trial conditions for moulding the expanded elastomers:

The press for injecting is equipped with a so-called valve-type closed nozzle enabling the blowing agent to be better mixed with the molten substance.

The plaque mould used for these trials possessed a 100 × 100 × 10 mm cavity. Additional vents were created on the parting line so as to make the rapid injection of the substance easier.

Injection was carried out via a 3 mm layer threshold.

The injection rate is 80% of the maximum rate, that is a rate of 200 $cm^3$/second. The holding pressure exerted was minimal.

Trial conditions for moulding the compact elastomers:

- Visumat 500 - Billion 140 L injection press
- 100 × 100 × 2 mm plaque mould
- 0.9 mm layer threshold
- Holding pressure: 30 bar
- Injection rate: 50%
- Mould temperature: 25°C.

Measurement of the cohesive force between the two materials was performed according to the NFT 76-112 (ISO 4578) standard and may be likened to the peel strength of assemblies of flexible materials on flexible materials.

The test specimens were obtained by cutting over moulded plaques into strips of 25 mm in width.

An incision was made to a depth of 10 mm at the junction of the compact and lightened materials so as to permit gripping between the jaws of the testing machine, the test specimen having to be perfectly aligned between the jaws so that the tensile load applied is uniformly distributed over its width.

The rate of movement of the jaws is 50 mm/min.; the peel forces are expressed in N/cm.

The examples which follow have the purpose of illustrating the invention without, however, limiting

it; Examples 1-5 illustrate the injection of the lightened material onto a compact elastomer insert, Examples 6-11 the overmoulding of a compact elastomer onto a lightened thermoplastic insert, with the special feature, in the last two (10-11), that lightening was achieved using an endothermic-type blowing agent.

The results of the various tests are set out in Tables 1 and 2.

**EXAMPLE 1**

The PEBAX MX 1205 insert was injection moulded, as a 100 x 100 x 2 mm plaque, at an injection temperature of 210°C.

Onto this insert, placed at the bottom of the 100 x 100 x 10 mm cavity, was injected, by overmoulding at a temperature of 190°C, the PEBAX MX 1205 polyether-block amide containing 0.6% of Genitron EPC blowing agent. The lightened PEBAX obtained had a density of 0.6 and possessed good adhesion to its thermoplastic insert. Cohesive failure was observed between the materials, with creep of the PEBAX MX 1205.

**EXAMPLE 2**

Elastollan 1185 A50 polyurethane was injection moulded at a temperature of 240°C in order to obtain a 100 x 100 x 2 mm insert onto which was injected, by overmoulding, PEBAX MX 1205 lightened by 0.6% of Genitron EPC.

Satisfactory adhesion between the insert and the foam was obtained, with adhesive failure between the materials.

**EXAMPLE 3**

The Hytrel 4056 compact thermoplastic copolyether (100 x 100 x 2 mm insert) was injection moulded at 200°C.

Onto this insert was injected, by overmoulding, PEBAX MX 1205 lightened by 0.6% of Genitron EPC blowing agent. A slightly weak adhesion was observed between the insert and the foam, with adhesive failure between the materials.

**EXAMPLE 4**

PEBAX 3533 polyether-block-amide compact thermoplastic (100 x 100 x 2 mm insert) was injection moulded at a temperature of 210°C.

After overmoulding with PEBAX MX 1205 lightened by 0.6% of Genitron EPC blowing agent, very good adhesion was obtained between the insert and the foam, characterized by a cohesive failure, then tearing of PEBAX 3533.

**EXAMPLE 5**

PEBAX 2533 lightened by 0.6% of Genitron EPC blowing agent was injected, by overmoulding, onto the same insert used in Example 1 and good adhesion was

obtained between the insert and the foam, with cohesive failure and tearing of PEBAX 2533.

**EXAMPLE 6**

PEBAX MX 1205 polyether-block-amide lightened thermoplastic (100 x 100 x 8 mm insert) was injection moulded at a temperature of 190°C.

The expansion obtained by 0.6% of Genitron EPC enabled a material density of 0.55 to be reached.

The Elastollan 1185 A50 compact elastomer was injection moulded at a temperature of 240°C onto this insert placed at the bottom of the 100 x 100 x 10 mm cavity.

Slight deformation of the lightened thermoplastic insert, due to the pressure exerted during the overmoulding of the compact elastomer, was observed; however, the adhesion between the materials remains very satisfactory, with cohesive failure and tearing of the PEBAX foam.

**EXAMPLE 7**

PEBAX 3533 was injected, by overmoulding, onto the same insert used in Example 6.

Good adhesion, with cohesive failure, was observed.

**EXAMPLE 8**

Polyetherurethane 1185 A50 was injected, by

overmoulding, onto a PEBAX 2533 insert lightened by 0.6% Genitron EPC.

Good adhesion of the material was obtained, the results of the tests being characterized by creep and tearing of the foam.

**EXAMPLE 9**

PEBAX 3533 was injected, by overmoulding, onto the same insert used in Example 8.

Good adhesion of the materials and peeling of the foam was obtained.

**EXAMPLE 10**

Elastollan 1185 A50 compact thermoplastic was injected, by overmoulding, onto the 100 × 100 × 8 mm insert of the PEBAX MX 1205 thermoplastic lightened by 1.2% of Genitron SIC 35/22 endothermic agent. Comments similar to Example 6.

The skin effect on the foam in no way impairs the adhesion of the materials and cohesive failure, with tearing of the foam, is observed.

**EXAMPLE 11**

PEBAX 3533 was injected, by overmoulding, onto the same insert used in Example 10; comments similar to Example 7.

1. OVERMOULDING OF THE LIGHTENED POLYETHER-BLOCK AMIDE ONTO A THERMOPLASTIC INSERT

| | Thermoplastic | | Blowing agent | Adhesion F. |
|---|---|---|---|---|
| Ex. | Insert (100 x 100 x 2 mm) | Lightened overmoulding | Ref % | N/cm |
| 1 | PEBAX MX 1205 | PEBAX MX 1205 | 0.6 GENITRON EPC | 18.5 |
| 2 | ELASTOLLAN 1185 A50 | PEBAX MX 1205 | 0.6 GENITRON EPC | 5.8 |
| 3 | HYTREL 4056 | PEBAX MX 1205 | 0.6 GENITRON EPC | 3.6 |
| 4 | PEBAX 3533 | PEBAX MX 1205 | 0.6 GENITRON EPC | 9.3 |
| 5 | PEBAX MX 1205 | PEBAX 2533 | 0.6 GENITRON EPC | 9.5 |

2. OVERMOULDING OF THE COMPACT THERMOPLASTIC ONTO A LIGHTENED POLYETHER-BLOCK AMIDE INSERT

| | Thermoplastic | | Blowing agent | Adhesion F. |
|---|---|---|---|---|
| Ex. | Lightened insert (100 x 100 x 8 mm) | Compact overmoulding | Ref % | N/cm |
| 6 | PEBAX MX 1205 | ELASTOLLAN 1185A50 | 0.6 GENITRON EPC | 19.5 |
| 7 | PEBAX MX 1205 | PEBAX 3533 | 0.6 GENITRON EPC | 12 |
| 8 | PEBAX 2533 | ELASTOLLAN 1185A50 | 0.6 GENITRON EPC | 3.5 |
| 9 | PEBAX 2533 | PEBAX 3533 | 0.6 GENITRON EPC | 7.4 |
| 10 | PEBAX MX 1205 | ELASTOLLAN 1185A50 | 1.2 GENITRON SIC 35/22 | 9.6 |
| 11 | PEBAX MX 1205 | PEBAX 3533 | 1.2 GENITRON SIC 35/22 | 16.2 |

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A bilayer article comprising a lightened thermoplastic elastomer of the polyetheramide type adhering, by itself, to a non-lightened thermoplastic.

2. Bilayer article according to 1, in which the non-lightened thermoplastic is chosen from polyetheramides, polyetheresters, polyurethanes.

3. Bilayer article according to 1, characterized in that the polyetheramides are polyetheresteramides obtained by polycondensation of aliphatic alpha,omega-dihydroxylated polyamide blocks.

4. Method of joining together, without adhesive, a lightened thermoplastic elastomer of the polyetheramide type and other non-lightened thermoplastics of the same kind or of a different kind, characterized in that the joining-together is performed in one operation during the injection of the second material onto the first, this having the function of an insert.

5. Shoe sole comprising a bilayer according to any one of Claims 1 to 3.

DATED this 10th day of October, 1996

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# ABSTRACT

A bilayer article comprising a lightened thermoplastic elastomer of the polyetheramide type adhering, by itself, to a non-lightened thermoplastic which may be chosen from polyetheramides, polyetheresters, polyurethanes.

The bilayer, obtained by overmoulding the lightened thermoplastic onto the compact thermoplastic, may be employed in the manufacture of shoe soles.

# INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/FR 94/01238

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B29C45/14 B32B27/24 A43B13/12 //B29K71:00,B29K77:00, B29K96:04,B29K105:20,B29L9:00,B29L31:50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B29C C08G A43B B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| Y | DATABASE WPI<br>Section Ch, Week 9305,<br>Derwent Publications Ltd., London, GB;<br>Class AEF, AN 93-039339 C05!<br>& JP,A,04 363 221 (NIFCO INC. & TORAY IND. INC.) 16 December 1992<br>see abstract<br>--- | 1,2,4,5 |
| Y | EP,A,0 235 396 (HULS A.G.) 9 September 1987<br>see the whole document<br>--- | 1,2,4,5 |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 15, no. 211 (C-0836) (4739) 29 May 1991<br>& JP,A,03 060 601 (ASAHI CORP.) 15 March 1991<br>see abstract<br>---<br>-/-- | 4,5 |

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 27 January 1995 | 23. 02. 95 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+ 31-70) 340-3016 | Authorized officer<br>Molto Pinol, F |

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | EP,A,0 060 240 (DISTROPAT A.G.) 15 September 1982<br>see the whole document<br>--- | 4,5 |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 14, no. 24 (C-677) (3967) 18 January 1990<br>& JP,A,01 265 901 (ASAHI CORP.) 24 October 1989<br>see abstract<br>----- | 4,5 |

# INTERNATIONAL SEARCH REPORT

information on patent family members

Inter nal Application No
PCT/FR 94/01238

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|---|---|---|---|---|
| EP-A-0235396 | 09-09-87 | DE-A- | 3606473 | 03-09-87 |
| | | JP-A- | 62212144 | 18-09-87 |
| | | US-A- | 4816345 | 28-03-89 |
| EP-A-0060240 | 15-09-82 | AT-A- | 386514 | 12-09-88 |
| | | US-A- | 4497123 | 05-02-85 |